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How do the Shape of Clay and Type of Modifier Affect Properties of Polymer Blends?

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ABSTRACT: Polyamide 6/ethylene–propylene–diene metallocene terpolymer/(ethylene–propylene–diene copolymer)-graft-(maleic anhydride) blends with clay (3 and 5 wt % depending on the formulation), different clays (montmorillonite and sepiolite) and different surface functionalization (ammonium salts and silanes) were studied to analyze the effect of the shape of clay and type of modifier on their properties. The results have shown that sepiolite has higher influence on the morphology and on the mechanical properties than montmorillonite. In that sense, blends with 3 wt % of sepiolite have reached the best balanced properties, i.e., tensile modulus and impact strength, than their homologous with montmorillonite. Furthermore, the blends with 3 wt % of sepiolite have reached the highest mechanical properties compared with blends with higher montmorillonite content. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: sepiolite; montmorillonite; blends; polyamide; clay shape

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INTRODUCTION

The addition of clay at low loadings to polymeric materials have been attracting great interest, because those materials leads to an improvement in several properties such as mechanical and permeability properties, fire retardancy and temperature resistance, among others.[1] This improvement is due to the high aspect ratio and because of the ability to intercalate the clay platelets. Also, the surface functionalization of the nanoparticles is another key issue to taking into account to obtain high intercalation and exfoliation into the polymeric matrix.[2]

In recent years, various nanoparticles have been used to improve the performance of polymers, including spherical silica,[3,4] layered silicates,[5,6] fibrous silicates,[7–9] carbon nanotubes,[10] as well synergetic effect between them.[11] The interaction between the primary particles of fibrous silicates is weaker than in the case of layered silicates[12]; consequently a better dispersion can be obtained on polymer nanocomposites and a higher improvement of the mechanical properties can be expected.

Sepiolite is a natural fibrous clay mineral with a typical molecular formula of $Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4{\cdot}8H_2O$. Sepiolite structure is composed of blocks of two tetrahedral silica sheets sandwiching an octahedral sheet of magnesium oxide hydroxide. The blocks are not sheets but ribbons which are linked forming an open channel similar to that of zeolites. This unique needle-like structure with interior channels (0.36 nm × 1.1 nm) allows a limited penetration of organic and inorganic cations. Because of the discontinuity of the external silica sheet, a significant number of silanol (Si—OH) groups are present at the surface of the sepiolite.[13]

Although there is a lot of work done in polymer nanocomposites, most of them showed that the properties related to rigidity are improved, while all those properties related to toughness are not, as was expected.[2] Nowadays, the development of new materials with balanced properties between stiffness and toughness are required in sectors such as automotive to develop some parts like bumpers, hub cups, tail gates, doors handle, etc. Thus, the addition of an elastomeric phase to polymer nanocomposites usually could improve the toughness, but a detrimental of the stiffness properties will be obtained.[14–21] Then, the challenge is to achieve a good balance between stiffness and toughness. In that sense, our research group has experience in developing polymer nanoblends and we have found that a good balance between stiffness, toughness, and heat temperature behavior seems to be reached when the EPDM-*g*-MA : MMT ratio is about 5 : 1.[22] In that work, the key issue was to achieve a

Table I. Experimental Conditions of Blending Extrusion for Blends

		Temperature profile (°C)									
Profile	Feed rate (kg h^{-1})	T1	T2	T3	T4	T5	T6	T7	T8	T9	Die
A	6	245	250								
B		145	200	230	250	250	250	250	240	235	230

good interaction between polymer components and a high montmorillonite exfoliation in PA6 matrix.

From our knowledge, all studies based on polymer nanoblends used clay with a platelet shape like smectite. Furthermore, the study of the microstructure and macrostructure of polymer blends with fibrilar clay shape, i.e., sepiolite, offers a unique opportunity to know how the properties are influenced by the shape of the clay.

In that sense, the aim of this work is to compare the effect of clay shape on polymer nanoblends based on PA6 and EPDM using montmorillonite or sepiolite modified with the same organic surfactant, in this case an ammonium salt. Also along this article, we will explore the effect of change the surfactant employed in sepiolite, because the modification degree of clay could affect both the inorganic/organic compatibility and the dispersion of the sepiolite in the polymer matrix. In that sense, the sepiolite employed was organically modified with silanes, because of the high affinity between silane groups and amide groups of PA6.[23]

Furthermore, in this article we have used a theoretical relation of EPDM-*g*-MA : clay 5 : 1, where the amount of clay (montmorillonite or sepiolite) was 3 or 5 wt %, because blends with that relationship showed good balanced properties for automotive parts as was explained in our previous work.[22] Then, with this study it will be established if the theoretical relation of EPDM-*g*-MA : clay 5 : 1,with these amounts of filler, may be applied with other types of clays such as sepiolite.

EXPERIMENTAL

Materials and Nanoblends Preparation

Polyamide 6 (PA6), commercialized as Akulon F130C supplied by DSM, was used as the matrix phase. The dispersed phase was an ethylene-propylene-diene metallocene terpolymer, (mEPDM) commercialized as Nordel IP3722P and supplied by Dupont. An ethylene-propylene-diene copolymer grafted with maleic anhydride (EPDM-*g*-MA Royaltuf 498 from Crompton), which contains 72.5 wt % ethylene, 0.95 wt % ENB, and 1 wt % maleic anhydride grafted, was used as a compatibilizer. An antioxidant Irganox B1171 (blend 1 : 1 of Irganox 1098 and Irgafos 168 from Ciba) was employed to diminish the effect of the temperature and compounding conditions in polyamide 6. This antioxidant was used to prepare a polyamide masterbatch, which was added in 0.2 wt % before blend preparation. The montmorillonite (MMT) used in this study was supplied by Süd Chemie with a trade name of Nanofil® 8. The surfactant used in this MMT was diasteryldimethyl-ammonium chloride (MMT-2M2HT). M and HT represent methyl and tallow-based product in which the majority of doubled bonds have been hydrogenated. The amount of modifier agent was a 45 wt % calculated by means of TGA. On the other hand, sepiolite clay (NS) was kindly supplied by TOLSA S.A. The sepiolite was modified by TOLSA S.A. with a protonated quaternary ammonium salt, specifically diasteryldimethyl-ammonium chloride (NS-2M2HT), and with amino-silane reagents by covalent bonding on surface silanols, specifically aminosilane (NS-HS06). The amount of modifiers of the sepiolite was 45 and 0.6 wt %, respectively.

Thermogravimetric analysis (TGA) was used to determine the clay content in the obtained nanocomposites. Thermograms were obtained in nitrogen atmosphere with a heating rate of 10°C min^{-1} using a Mettler Toledo TGA851. At least five values of different samples were taken to assure the content of clay.

Nanoblends were prepared in a Leistritz corrotating twin-screw extruder ($L/D = 27$, $L = 972$ mm) at a temperature profile described in Table I. The screw speed was fixed at 145 rpm and the feed rate was 6 kg h^{-1}. Two-steps blending sequence was employed for the preparation of nanoblends. In the first step, PA6/OMMT nanocomposite was prepared, with *A* temperature profile, and then mixed with the elastomeric compound in a second step, with *B* temperature profile. The nanoblends obtained were injection molded into test pieces for mechanical tests by using an injection molding machine (Margarite JSW110). The temperature of the cylinders was 230–250°C and the mold temperature was 80°C. The nanoblends were obtained as in our previous work to do comparisons.[22] Before the melting processing step, the PA6, the clay, and the nanoblends were dried at 80°C for 24 h in an oven.

The compositions depend on the amount of clay because as can be seen in our previous work, the theoretical relation EPDM-*g*-MA : clay 5 : 1 have reached the best balanced properties in blends of PA6/mEPDM/EPDM-*g*-MA/clay with composition 75-*x*/25-*y*/*y*/*x*.[22] Therefore, if there is 3 wt % of clay, the nanoblend composition is PA6/mEPDM/EPDM-*g*-MA/Clay (72/10/15/3); nevertheless if there is 5 wt % of clay, the nanoblend is PA6/EPDM-*g*-MA/Clay (70/25/5). With each composition, motmorillonite modified with 2M2TH and sepiolite modified with 2M2TH and HS06 has been employed to compare the effect of change of the shape of the clay, and with sepiolite, the effect of change of the modifier. The compositions of the six blends are shown in Table II.

Transmission and Scanning Electron Microscopy (TEM, SEM)

The dispersion of the clay in the polymers was evaluated by using transmission electron microscopy, TEM, Jeol JEM 2000FX electron microscope with 200 kV accelerating voltage. Ultrathin sections of the nanocomposites with a thickness of about 100 nm were prepared with a Reichert-Jung Ultracut E ultramicrotome equipped with a diamond knife in a liquid nitrogen

Table II. Composition of Nanoblends

Sample	MMT-2M2HT (wt %)	NS-2M2HT (wt %)	NS-HS06 (wt %)
PA6/mEPDM/EPDM-*g*-MA/MMT-2M2HT	3	0	0
PA6/mEPDM/EPDM-*g*-MA/NS-2M2HT	0	3	0
PA6/mEPDM/EPDM-*g*-MA/NS-HS06	0	0	3
PA6/EPDM-*g*-MA/MMT-2M2HT	5	0	0
PA6/EPDM-*g*-MA/NS-2M2HT	0	5	0
PA6/EPDM-*g*-MA/NS-HS06	0	0	5

Only the inorganic material is considered. The compositions are expressed as a ratio of PA6/mEPDM/EPDM-*g*-MA/clay, that is, 75-*x*/25-*y*/*y*/*x* where EPDMgMA:Clay is 5 : 1.

environment. A Hitachi S3400 scanning electron microscope was used to research the rubber particle size and particle size distribution. The injection-molded specimens were broken cryogenically in liquid nitrogen and the elastomeric phase was extracted from the surface by etching with boiling xylene during at least 6 h. After sputter coating with a thin film of gold, the specimens were examined. An accelerating voltage of 20 KV and a magnification range from 1300× to 10,000× was used.

Mechanical and Thermo Mechanical Testing

Tensile properties were measured according to UNE-EN ISO 527-1 and 527-2 with an Instron Model 5500R6025. Modulus was determined at a crosshead rate of 1 mm min^{-1} while tensile strength and elongation at break were collected at 10 mm min^{-1}.

Notched Izod test was performed at temperatures of 25 and −30°C on a Ceast Resil Impactor according to the ISO 180:2000 standard equipped with a thermal chamber. The average values were calculated from seven runs for each sample. Heat deflection temperature (HDT) was determined in an HDT-VICAT tester microprocessor (CEAST 6911.000) according to UNE-EN ISO 75-1 and using a load of 1.8 MPa.

RESULTS AND DISCUSSION

Morphological Analysis

The dispersions of clay and rubber particle size distribution are fundamental issues to understand the mechanical properties of nanoblends. To know how both the rubber phase and clay are distributed, in Figures 1 and 2 are shown the SEM and TEM microphotographs. Furthermore, in Figure 1 the rubber average particle size can be seen.

As can be seen, in the top and left of the Figures 1(a) and 2(a), the change of the shape of the clay affects the distribution of the rubber particles, but the effect is different depending on blend composition. In that sense, in blends with 3 wt % of clay, the change of the shape provokes a heterogeneity in the rubber particle size distribution, because of blends with platelet-like fillers have achieved an average in the rubber particle size of 0.29 ± 0.09 μm, while those blends with needle-like fillers have an average of 0.24 ± 0.16 μm.

On the other hand, blends with composition PA6/EPDM-*g*-MA/Clay, i.e., with 5 wt % of clay, have shown a decrease in the rubber particle size if the clay employed is needle-like fillers instead of platelet-like fillers. The rubber particle size, in micrometers, is 0.14 ± 0.04 and 0.29 ± 0.09, respectively. This behavior could be attributed to the shape of the sepiolite, because fibers may break the rubber particles due to the shear induced in the extrusion process.

Attending on the organic modification of the sepiolite, it can be seen that in blends with 3 wt % of clay, the rubber particle size is smaller when the sepiolite is modified with silanes [Figure 1(a3)] instead of ammonium salts. The lower is the amount of modifier, the higher is the presence of Si—OH group that have not been protected and could interact with polar groups leading to smaller rubber particle size. On the other hand, blends with 5 wt % of NS have shown almost the same rubber particle size as can be seen in Figure 2(a2,a3), indicating that the presence of only one type of elastomeric phase (EPDM-*g*-MA) governs the morphology of the blends.

The change in the shape of the clay can be observed in the TEM microphotographs showed in Figures 1(b) and 2(b). In all blends, independently of the shape of clay, particles of clay well dispersed as well as some stacked MMT are presented,[22] also some agglomerates of sepiolite can be seen. Nevertheless, the defibrillation of the sepiolite is different depending on the surfactant employed and on the composition of the blend. For example, while in blends with 3 wt % of sepiolite [Figure 1(b2,b3)], there are less aggregates when it is modified with ammonium salts (2M2HT) than when it is modified with silane groups. Nevertheless, blends with 5 wt % of sepiolite have shown an opposite behavior as can be observed in TEM microphotographs showed in Figure 2(b2,b3), i.e., those blends with NS-HS06 have shown more separated needles than those with NS-2M2TH. This is related to the polarity of the organic modifier due to ammonium salts are less polar than silanes and PA6/EPDM-*g*-MA/clay has higher polarity than PA6/mEPDM/EPDM-*g*-MA/clay.

Mechanical and Thermo Mechanical Properties

The mechanical properties, tensile modulus (E) and heat deflection temperature (HDT) are shown in Figure 3 because both properties are related to rigidity.[24] To better understand the plot, it can be seen in the left and in the right the tensile modulus of blends containing 3 and 5 wt % of clay, respectively. Thus, in the middle of the plot, it can be seen the heat

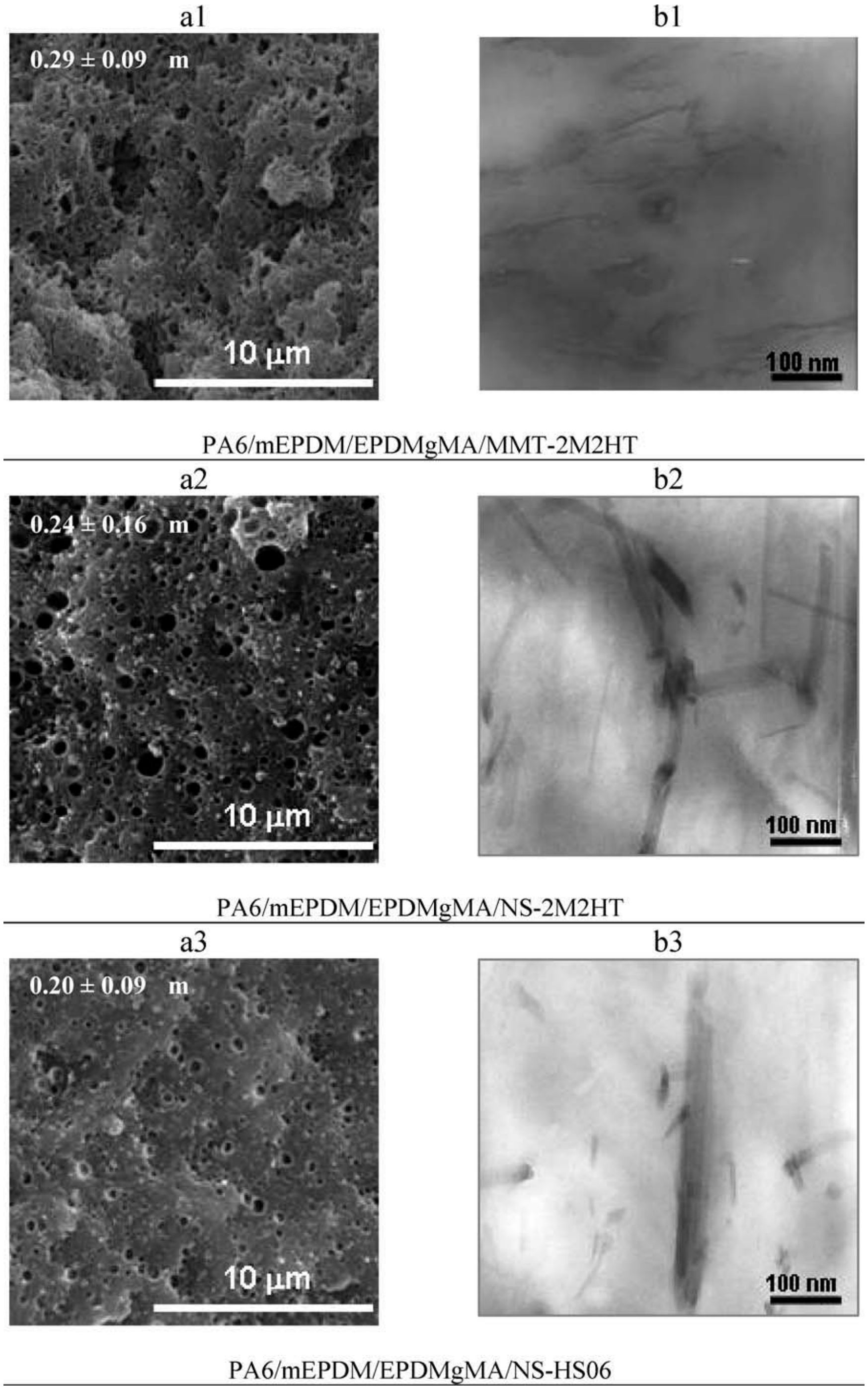

Figure 1. Rubber particle size, SEM, and TEM microphotographs, left and right, respectively, of nanoblends with 3 wt % of clay.

deflection temperature, in the left the results of blends with composition PA6/mEPDM/EPDM-*g*-MA/clay and in the right those related to blends with composition PA6/EPDM-*g*-MA/clay.

In the same way, Figure 4 showed the yield stress (σ_y) and the impact strength (I_s) at −30°C of both pairs of blends, because both properties are related to the interaction between the filler and the polymer.[25] Finally, in Figure 5 are shown the properties related to the adhesion between polymer phases, i.e., the elongation at break (ε_b) and the impact strength (I_s) at room temperature.[26]

As can be seen in Figure 3, the Young's modulus of nanoblends with 3 wt % of clay is affected by the clay shape. In that sense, nanoblend with NS-2M2HT has shown an increase of 8%, compared to blend reinforced with montmorillonite. These blends have been injection molded and that causes the orientation of the clays within polymer matrix. As Billoti et al.[27] have stated in their study, in unidirectional composites, fibres are more

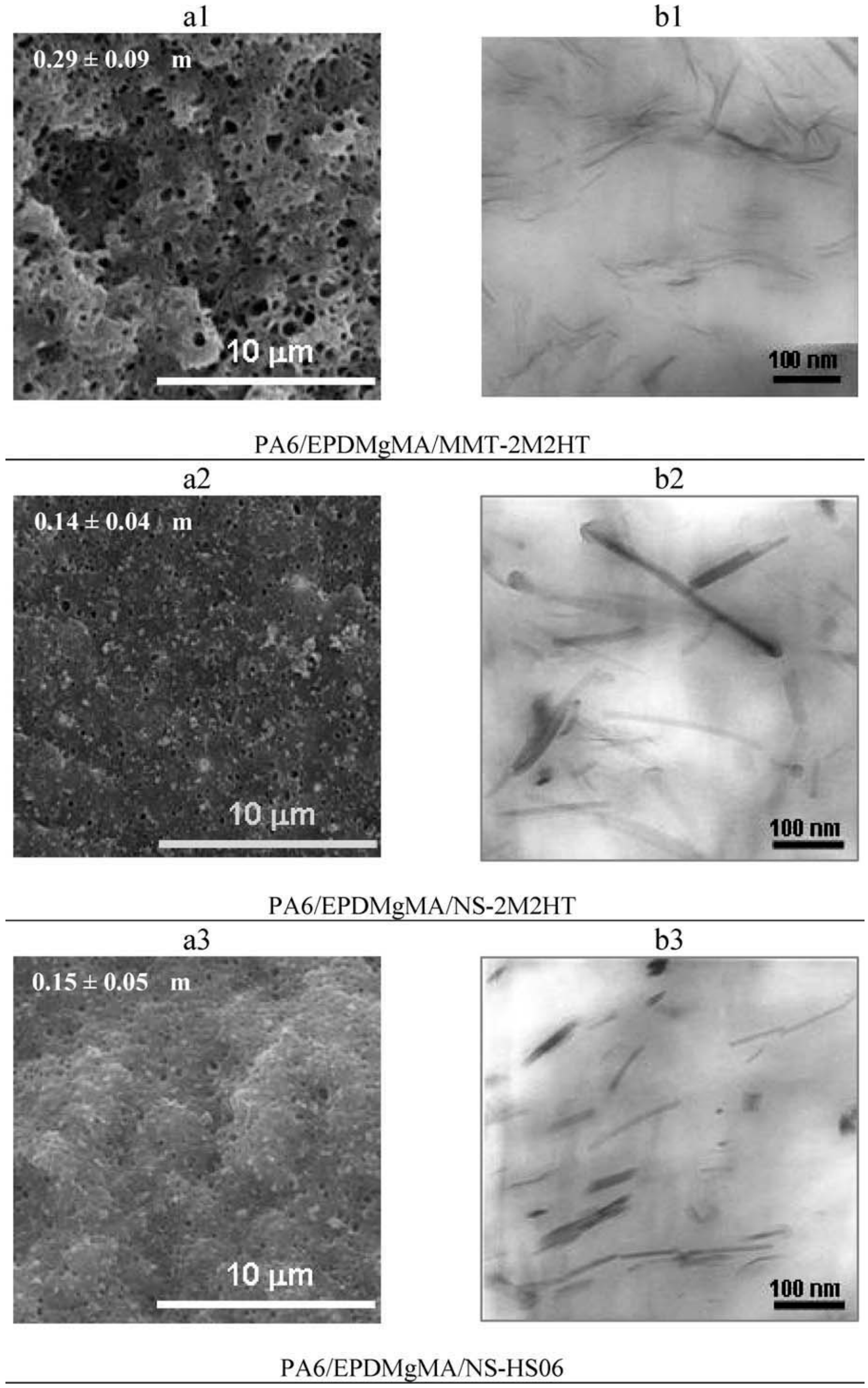

Figure 2. Rubber particle size, SEM and TEM microphotographs, left and right, respectively, of nanoblends with 5 wt % of clay.

effective than platelets because fiber-like fillers approach this maximum reinforcement level already for aspect ratios of 100, while platelet-like fillers demand aspect ratios exceeding 2000.

Nevertheless, attending to the modifier present in the sepiolite, when silane is present, the modulus decrease a 2% compared to blends with NS-2M2TH. This behavior is because the NS-2M2HT has showed a better dispersion than NS-HS06 as can be seen in TEM microphotographs showed in Figure 2 and also because, higher is the amount of modifier the greater is the mechanical properties reached.[9] Furthermore, it is interesting to notice that tensile modulus of PA6/mEPDM/EPDM-*g*-MA/NS-HS06 is still higher than modulus of PA6/mEPDM/EPDM-*g*-MA/MMT-2M2HT indicating that independently of the type of modifier present in the sepiolite, fibres are more effective than platelet-like fillers.

On the other hand, if the clay shape is compared in nanoblends containing 5 wt % of clay (PA6/EPDM-*g*-MA/Clay), those with MMT-2M2TH have shown tensile modulus 2% higher than

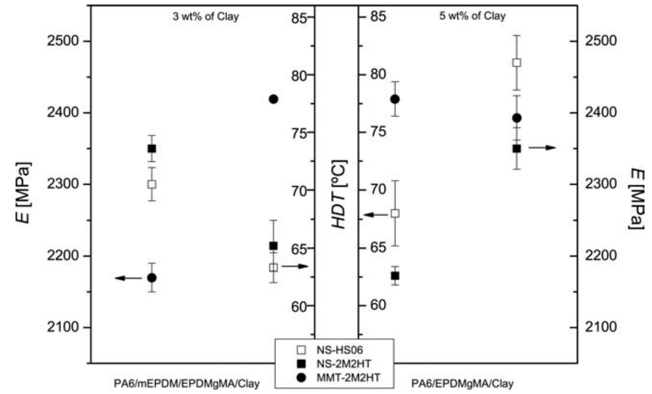

Figure 3. Modulus (*E*) and heat deflection temperature (HDT) of nanoblends depending on EPDM-*g*-MA content.

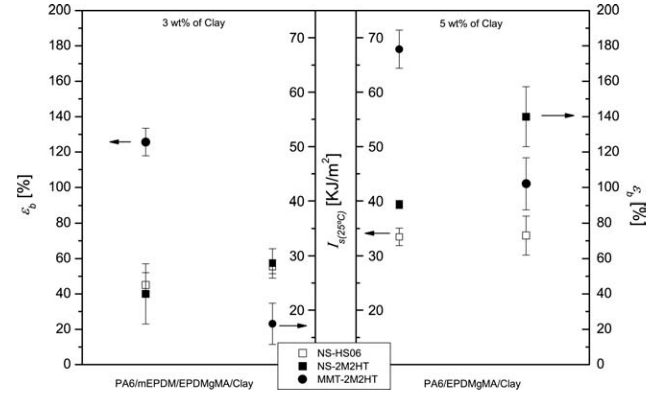

Figure 5. Elongation at break (ε_b) and impact strength (I_S), at 25°C, of nanoblends depending on EPDM-*g*-MA content.

those blends with NS-2M2TH. This slight increment could be due to the better dispersion of MMT as was explained above in the TEM microphotographs (the XRD patterns of the nanoblends containing MMT could be seen in a previous paper).[22] Nevertheless, attending to the type of modifier present in sepiolite, the highest modulus was achieved in blends with NS-HS06. This sepiolite presents higher affinity with blends components, than NS-2M2TH, because of the polar groups present in the blend.[27]

The heat deflection temperature is also a property related to the rigidity of blends, and it is a key parameter in the automotive industry because it relates the maximum temperature at which those materials can be used. In that sense, the HDT should be in accordance with Young's modulus values. Nevertheless, in this study this is not totally true because the change in the shape of the clay have shown a different trend, i.e., the HDT value in blends with MMT-2M2HT is 3 and 20% higher than blends with NS-2M2HT, when the composition was PA6/mEPDM/EPDM-*g*-MA/clay and PA6/EPDM-*g*-MA/clay, respectively. Similar trend has been observed by Xie et al.[28] in PA6 nanocomposites. In those materials, the highest value of Young's modulus was achieved in nanocomposites with sepiolite, while the best HDT value was obtained in those nanocomposites with MMT. On the other hand, the change in the organic modifier of the sepiolite already have the same effect in HDT than in

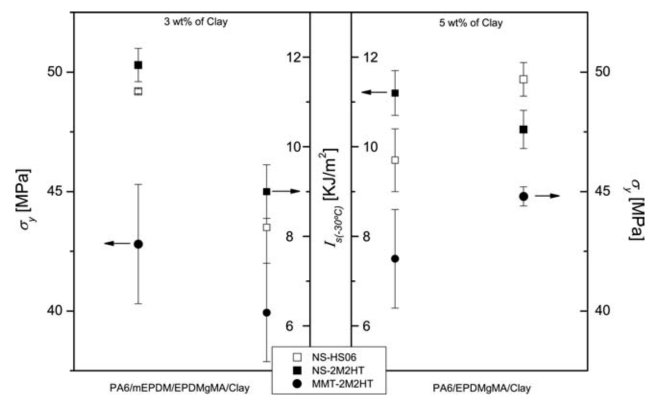

Figure 4. Yield stress (σ_y) and impact strength (I_S), at −30°C, of nanoblends depending on EPDM-*g*-MA content.

Young's modulus, i.e., in blends with 3 wt % of NS, the greater values of Young's modulus and HDT were achieved with the modifier 2M2TH, while in blends with 5 wt %, the best result was achieved with the modifier HS06.

As was mentioned above, the yield stress and the impact strength are related to the adhesion between the filler and the polymer as well as to the stiffness of the material. In that sense, as can be seen in Figure 4, independently of blend composition, i.e., PA6/mEPDM/EPDM-*g*-MA/clay or PA6/EPDM-*g*-MA/clay, the NS promotes a 17 and 6% higher yield stress than MMT, respectively, indicating that filler interaction is greater with fibrous clay than with laminar clay as was stated by Bilotti et al.[27] These authors attribute this behavior to the strong hydrogen bonding between silanol groups on the sepiolite surface and amide groups of the matrix, which are weaker in MMT, even after surface treatment in both clays. Nevertheless, attending to the modification of the nanosepiolite, blends with 3 wt % of clay presented 2% higher σ_y when the NS-2M2HT is employed, while in blends with 5 wt %, the best σ_y value was observed in blends with NS-HS06 due to the different polarity of blends and modifiers as was explained above. The impact strength at low temperature has shown the same trend as yield stress as can be seen in Figure 4. Independently of blend composition, i.e., blends with 3 or 5 wt % of clay, those with sepiolite have increased almost a 45% the impact strength compared to blends with montmorillonite.

Nevertheless, the change of the modifier of the sepiolite has the same effect in both pair of blends, i.e., independently of blend composition, PA6/mEPDM/EPDM-*g*-MA/clay or PA6/EPDM-*g*-MA/clay, blends with sepiolite modified with 2M2TH have promoted an increase of 12% on the impact strength compared to those blends with nanosepiolite modified with HS06. This is due to high amount of modifier that prevents the reaction among Si—OH of sepiolite and polar groups of PA6, improving the reaction between the MA groups present in the elastomeric phase with the amine end groups of the polyamide; which is the main factor involved in the improvement of impact strength at low temperatures.[29]

There are several factors involved in the change of the elongation at break (ε_b),[29] the rubber particle size, the "network" effect induced by the presence or the EPDM-*g*-MA and the presence of the clay. In that sense, the trend of the elongation at break is agreed with the results of modulus obtained as it can be observed if it is compared with Figures 3 and 5, i.e., the higher is the stiffness, the lower is the elongation at break.

The impact strength of nanoblends at 25°C is also shown in Figure 5. Blends reinforced with 3 wt % of clay, PA6/mEPDM/EPDM-*g*-MA/clay, have shown that fibrous clay improves the I_S in a 65% respect to those with MMT. On the other hand, if the modifier of the sepiolite is changed, the impact strength was almost the same.

Nevertheless, blends with 5 wt % of clay showed better impact strength at room temperature if the clay used is MMT-2M2TH instead of NS-2M2TH. This behavior is caused by the rubber particle size achieved in those blends, 0.29 and 0.14 μm, respectively, because an increase in Izod impact strength of a thermoplastic PA6 blend is only achieved when the rubber particle size is between 0.2 and 1 μm [Figure 2(a2,a3)].[29] If the modifier is changed on sepiolite clay, blends with clay modified with 2M2TH have shown an increase of 17% in the impact strength compared to those blends with sepiolite modified with HS06. This behavior is due to the excess of modifier present in NS-2M2TH, which has promoted a better interaction between the components of the blends, compared to blends with NS-2HS06, resulting in higher impact strength.

CONCLUSIONS

Is it really true that the shape of clay and modifier influences the properties of a blend? Well, along this article, it was observed that sepiolite has a lot of influence, not only in the morphology, but also in the mechanical properties.

The aim of the article was to compare the effect of the shape of the clay and the type of modifier present in sepiolite and to prove if the theoretical relation EPDM-*g*-MA : clay 5 : 1 could be applied with other types of fillers such as sepiolite.

In that sense, attending to the shape of clay, in blends with PA6/mEPDM/EPDM-*g*-MA/clay, i.e., 3 wt % of clay, those with sepiolite have reached the highest balanced properties. An increment of 8, 20, and 45% was achieved in Young's modulus, yield stress, and impact strength at low temperature, respectively, while a decrease of 16 and 68% in HDT and impact strength at room temperature, respectively was found, compared to those blends with MMT. Nevertheless, with this blend composition, the change of the modifier in the sepiolite seems not to affect significantly the mechanical properties.

Furthermore, the blend with composition PA6/mEPDM/EPDM-*g*-MA/NS-2M2TH (72/10/15/3) has shown best mechanical properties than blends with higher MMT content, as it could be compared with our previous work in which PA6/mEPDM/EPDM-*g*-MA/MMT blends with different amounts of clay were studied.[22]

On the other hand, in blends with PA6/EPDM-*g*-MA/clay composition, i.e., 5 wt % of clay, the best balanced properties, among using sepiolite or MMT, were achieved in those blends with MMT, indicating that the relationship EPDM-*g*-MA : MMT found in our previous work is not valid for fibrous clays as sepiolite.

In reference to the surface functionalization of sepiolite, the blends reinforced with 5 wt % of sepiolite modified with silanes have reached better properties than those reinforced with sepiolite modified with ammonium salts. This indicates that the Si—OH groups of sepiolite, interact with the amide groups of the matrix and this improves the stiffness of the blends with a slight loss in toughness.

Finally, although this study has shown a part of the work based on the influence of the shape of clay and type of modifier on polymer nanoblends, it has found that best balanced properties could be reached with lower inorganic content, i.e., blends with fibrous clay are lighter materials with better properties than their homologous with MMT, which is an advantage for the automotive industry. Also, it has been observed that the relationship EPDM-*g*-MA : clay 5 : 1 obtained in PA6/EPDM/EPDM-*g*-MA/MMT with composition 75-*x*/25-*y*/*y*/*x*, it is only valid for MMT and it should not be extrapolated to other nanofillers such as sepiolite.

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